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(54) [Title of the Invention] Heat resistant member

(57) [Abstract]

[Constitution] A heat resistant member that formed a heat resistant film of a coating that consists of polyborosiloxane resin and the like heat resistant polymer and inorganic filler, characterized in that an amorphous thin film was provided by means of the baking of an organic acid metal salt on the base material.

[Effect] Greatly improves the anti-corrosion capacity of the base material, while maintaining the heat resistance performance of the coating well, and the coating does not flake from the base material, even if heated for a long time at a high temperature.

[Claims]

[Claim 1] A heat resistant member characterized in that an amorphous thin film was provided on a base material by means of the baking of organic acid metal salt, and on that, a heat resistant coating was provided by the application and baking of a coating material with inorganic filler and one or two types or more of resin selected from a group consisting of polyborosiloxane resin, polycarbosilane resin, polysilastyrene resin, polytitanocarbosilane resin, polysilazane resin caused to be dissolved or dispersed in a solvent.

[Detailed Description of the Invention]

[0001]

[Industrial Field of Application] The present invention relates to an improvement of a heat resistant member that has applied a heat resistant resin cover of polyborosiloxane resin and the like, and more particularly to a heat resistant member that has caused the anticorrosion property with respect to a base material to improve.

[0002]

[Prior Art] Accompanying the rapid development of technology of recent years, a heat resistant member that can be used in a high temperature region that exceeds 300° C has been desired in a broad range of areas, and various types of materials are being developed in order to form this kind of heat resistant member. As specific uses, there are the members of the inner and outer walls of various cooking devices, automobile engine peripheral parts and the like, and the present applicant has developed and already come to propose (for example, Japanese Patent Application Laid-open No. S63-291962) a cover body that mixed various types of fillers with polyborosiloxane resin as the main component and provided a film consisting of a heat resistant coating material dissolved or dispersed in a solvent on a metal and the like base material.

[0003] However, as for a film based on a coating material that makes polyborosiloxane resin the main component, although the heat resistance is sufficient, the film that can be obtained is semi-inorganic and cannot avoid the production of a microscopic pin hole, and this pin hole increases

in accordance with being used at a high temperature, and has sometimes passed through from the film side as far as the base material. As a result of this there have been the problems that gas and liquid easily contact the base material and rust is easily produced, and eventually flaking of the film is brought about.

[0004]

[Problems that the Invention is to Solve] In view of the points mentioned above, the present invention aims to provide a heat resistant member with superior durability that improves the anticorrosion capacity of the base material, and consequently prevents the flaking of the coating, in a heat resistant member having a heat resistant coating based on polyborosiloxane resin and the like.

[0005]

[Means of Solving the Problem] The present invention, namely, relates to a heat resistant member characterized in that an amorphous thin film was provided on a base material by means of the baking of organic acid metal salt, and on that, a heat resistant coating was provided by the application and baking of a coating material with inorganic filler and one or two types or more of resin selected from a group consisting of polyborosiloxane resin, polycarbosilane resin, polysilastyrene resin, polytitanocarbosilane resin, polysilazane resin caused to be dissolved or dispersed in a solvent.

[0006] In the present invention, since an amorphous thin film is provided by means of the baking of an organic acid metal salt on a base material, the base material surface is completely covered, barrier performance with respect to gas and liquid is improved, and corrosion and rust of the base material can be prevented. Furthermore, this amorphous thin film's adhesion to the heat resistant coating also is good and improves the overall durability of the heat resistant member.

[0007] The amorphous thin film based on the baking of organic acid metal salt in the present invention is an amorphous thin film that regards silica (SiO_2) and alumina (Al_2O_3), that can be obtained by heating that which dissolves at a comparatively low temperature among the organic acid salts of metal such as silicon and aluminum at a temperature of approximately $150 \sim 500^\circ \text{C}$, as the film forming substance. Specifically, there are octyl acid silicon, octyl acid

aluminum, naphthenic acid silicon, naphthenic acid aluminum and the like. These organic acid metal salts can form a film using heating and baking after being dissolved or dispersed in the appropriate solvent (ethanol, xylene, toluene and the like) and applied by means of flow coat and the like, or the CVD method and the like.

[0008] In the present invention a heat resistant coating is formed through the above-mentioned amorphous thin film. The resins of the coating material that forms the heat resistant coating are polyborosiloxane resin, polycarbosilane resin, polysilastyrene resin, polytitanocarbosilane resin, and polysilazane resin, and these are polymers that have silane, titanium, boron and the like metal elements in the main chain, and a methyl group, a phenyl group and the like organic groups bonded to the side chains. It is desirable to use 50 weight % or more of these resins in the total resin component in the coating material singly or as a mixture of two types or more. When the percentage of these resins is 50 weight % or less in the total resin component in the coating material, the heat resistant effect of the present invention cannot be sufficiently obtained. Furthermore, in the present invention silicon resin can be used at the same time in a range of 50 weight % or less in the resin portion. Polyborosiloxane resin, polycarbosilane resin, polysilastyrene resin, polytitanocarbosilane resin and polysilazane resin normally are heated and baked under anoxia and form a nonoxide system ceramic coating (SiC , B_4C_3 and the like), but by baking in the air, the organic groups of the side chains detach and, finally, because a thin ceramic coating of an oxide system forms, become a coating that is superior in heat resistance and impact resistance.

[0009] Furthermore, in the present invention inorganic fillers are blended in the above-mentioned resin with the object of causing further improvement of heat resistance. As inorganic fillers, oxide system inorganic fillers, for example, Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MnO_2 , WO_2 , NiO , CoO , CuO , MoO_3 , Fe_2O_3 , La_2O_3 , Bi_2O_3 , V_2O_3 , Pr_6O_{11} , AlN , SiC and, moreover, coloring pigments based on composite oxides of multiple metals and the like are exemplified, and these can be used singly or mixed. As for these inorganic fillers, it is desirable to mix 10 ~ 300 parts by weight with respect to 100 parts by weight of one type or two types or more of the resin part selected from a group consisting of polyborosiloxane acid, polycarbosilane resin, polysilastyrene resin, polytitanocarbosilane resin, and polysilazane resin. When too much inorganic filler is

added the thickness of the coating becomes uneven, and the viscosity of the coating material increases and workability deteriorates.

[0010] And the coating material is manufactured by causing the above-mentioned ingredients to be dissolved or dispersed in a solvent of toluene, xylene, solvent naphtha and the like, or mixing and sufficiently agitating that which was caused to be dissolved or dispersed in the same kind of solvent in advance and made into a liquid form.

[0011] The heat resistant member of the present invention, after the base material has been treated, if necessary, and after the above-mentioned organic acid metal salt has been baked in the appropriate thickness and formed an amorphous thin film, is manufactured by applying the coating material manufactured as mentioned above by the usual methods of spray coat, flow coat, dip coat, roll coat and the like, and baking this at a temperature of 400 ~ 450° C.

[0012]

[Embodiment] Embodiments of the present invention will be explained.

[0013] Embodiment 1

On a brass plate base material of a thickness of 0.8 mm, octyl acid aluminum dissolved in a solvent was applied by flow coat, baked at 500° C, and formed an amorphous thin film. On this a coating material obtained by mixing each ingredient by the blend shown in the table was applied by spraying, baked for 10 minutes at 400° C, formed a heat resistant coating and manufactured a heat resistant member the entire film thickness of which is 35 μ m. Using the heat resistant member obtained, pencil hardness, adhesion (tape-peeling test), heat resistance (coating state after 600° C x 24 hours heating), salt water spray resistance (state after spraying 5% salt water for 168 hours), acid resistance (coating state after being immersed for 72 hours in a 5% sulfuric acid solution), and alkali resistance (coating state after being immersed for 72 hours in a 5% sodium hydroxide solution) were tested. The results are shown in a table.

[0014] Embodiment 2

On a brass plate base material of a thickness of 0.8 mm, naphthenic acid silicon formed a film by the CVD method and formed an amorphous thin film. On this a coating material obtained

by mixing each ingredient by the blend shown in the table was used and a heat resistant member was manufactured the same as in Embodiment 1 and tested in the same way. The results are shown in a table.

[0015] Comparative example 1 ~ 2

On a brass plate base material of a thickness of 0.8 mm a coating material of a blend shown in the table was directly sprayed and applied, baked for 10 minutes at 400° C and formed a coating of 35 µm. Using this the same tests as Embodiment 1 were done. The results are shown in a table.

[0016]

Table 1

		Embodiment		Comparative Example	
		1	2	1	2
Blend	Borosiloxane resin	100	70	100	70
	Silicone resin		30		30
	Alumina	30	30	30	30
	Silica		20		20
	Titanium oxide		10		10
	Magnesium oxide	30		30	
	Black pigment	50		50	
	Solvent	130	100	150	100
Characteristics	Pencil hardness	4H	4H	4H	4H
	Adhesion	8 points	8 points	8 points	8 points
	Heat resistance	Good	Good	Flaking	Flaking
	Salt water spray resistance	Rust *1	Rust *1	Flaking	Flaking
	Acid resistance	Discoloration	Discoloration	Flaking	Flaking
	Alkali resistance	Softening	Softening	Flaking	Flaking

*1 ... Rust occurred in the vicinity of the cross-cut

[0017]

[Effects of the Invention] The heat resistant member of the present invention, while satisfactorily maintaining the heat resistance of a coating, greatly improves the anticorrosion performance of the base material and, even if heated for a long time at a high temperature, the coating does not flake from the base material.